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Adsorption of Block Copolymers from Nonselective Solvent

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The rational design of diblock copolymers for stabilization of colloidal dispersions requires a knowledge of the optimum sizes of both the anchor (A) and bouy (B) blocks to give the greatest surface density and adsorbed layer thickness. In the past few years two scaling models for diblock copolymer adsorption have appeared and these have been found to be in good agreement with experimental measurements of the adsorbed layer thickness and adsorbed amount, viz., the model of Marques and Joanny[1] (MJ model) for copolymer adsorption from a nonselective solvent and the model of Marques, Joanny, and Liebler[2] (MJL model) for copolymer adsorption from a selective solvent. The former model has been used to explain the surface force[3] and adsorbed amount[4] measurements of poly(ethylene oxide)-*b*-polystyrene (PEO/PS) adsorbed on mica from toluene, a good solvent for both blocks, while the MJL model has been found to be in good agreement with measurements of the adsorbed amount of poly(2-vinylpyridine)-*b*-polystyrene (PVP/PS) adsorbed on silicon from toluene,[5] a good solvent for polystyrene but a poor solvent for poly(2-vinylpyridine). A salient feature of the MJ and MJL models is that the scaling laws incorporate the dependences of the surface density and layer thickness on the sizes of both blocks of the copolymer.

Recently, Wu et al.[6] have presented the results of a study of the effect of the anchor and bouy block sizes on the adsorbed amount and hydrodynamic layer thickness in diblock copolymer adsorption. The copolymer studied was poly[(dimethylamino)ethyl methacrylate] (DMAEM)-*b*-poly(*n*-butyl methacrylate) (BMA) adsorbed on silica from 2-propanol, a good solvent for both blocks. In this copolymer, the DMAEM block interacts strongly with the silica surface while the BMA block was found to be nonadsorbing. Two series of materials, one having a total degree of polymerization $N_T = 200$ and the other having $N_T = 700$, were studied. Wu et al. compared their results with the self-consistent-field model of Evers et al.[7-9] and found, as predicted by this model, that the layer thickness and adsorbed amount passed through maxima although the positions of the experimentally observed maxima occurred at a lower fraction of DMAEM than predicted by the model of Evers et al.

In this paper we show how the scaling model of Marques and Joanny (MJ) for diblock copolymer adsorption from a nonselective solvent can be used to explain the results of Wu et al. and conversely how the results of Wu et al. (and our own work with PEO/PS block copolymers) illustrate the validity of the MJ model and point out its utility in the design of diblock copolymers for optimum stabilizing power. As with the model of Evers et al., the MJ model predicts a maximum in the adsorbed amount and the adsorbed layer thickness and gives a simple expression for the composition of the copolymer at this maximum for a given total degree of polymerization.

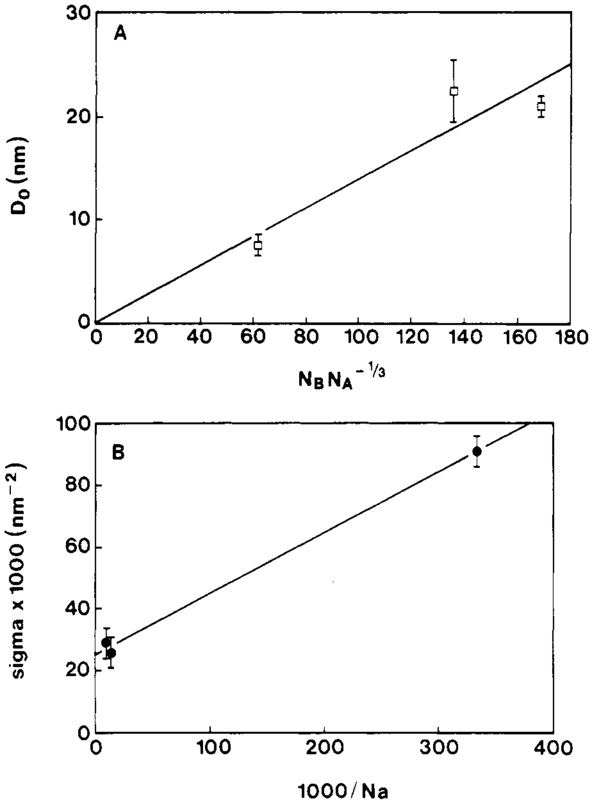

Figure 1. For regime I, plots of (A) the hydrodynamic thickness (D_0) of the adsorbed layer vs $N_B N_A^{-1/3}$ and (B) the surface coverage (σ) against $1/N_A$.

The model of Marques and Joanny gives expressions for the surface density σ in terms of the degrees of polymerization N_A and N_B of the anchor and bouy blocks, respectively. When both blocks are in a good solvent, a characteristic asymmetry ratio $\beta = (N_B/N_A)^{3/5}a'$ can be defined in terms of the Flory radii of the component polymers and a' is the ratio of the monomer sizes. The adsorption behavior of the copolymer depends on this asymmetry ratio as

$$\sigma \sim N_A^{-1} \quad \text{for } \beta < N_A^{1/2} \tag{1}$$

and

$$\sigma \sim \beta^{-2} \quad \text{for } \beta > N_A^{1/2} \tag{2}$$

The adsorbed layer thickness then follows from the Alexander–de Gennes[10,11] expression

$$L = N_B \sigma^{1/3} \tag{3}$$

giving

$$L = N_B N_A^{-1/3} \quad \text{for } \beta < N_A^{1/2} \tag{4}$$

and

$$L = N_B^{3/5} N_A^{2/5} \quad \text{for } \beta > N_A^{1/2} \tag{5}$$

We will denote the $\beta < N_A^{1/2}$ behavior as regime I and the $\beta > N_A^{1/2}$ as regime II. We have recently verified that the MJ scaling behavior for regime I is obeyed.[3]

Since the MJ model gives scaling laws for the surface density, we can convert the adsorbed amounts to surface

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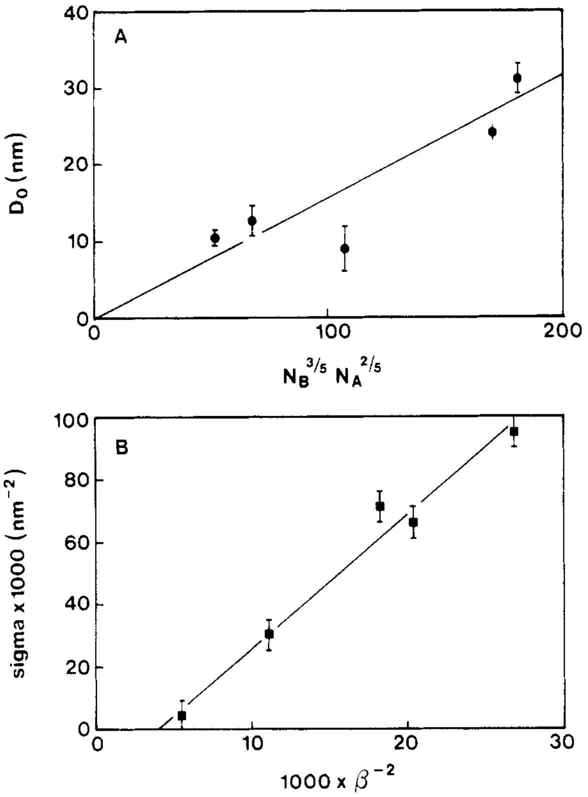

Figure 2. For regime II, plots of (A) the hydrodynamic thickness (D_0) of the adsorbed layer vs $N_B^{3/5}N_A^{2/5}$ and (B) the surface coverage (σ) against $1/\beta^{-2}$.

density using

$$\sigma = (\text{adsorbed amount}/M_w)N_{Av} \times 10^{-21} \qquad (6)$$

where the adsorbed amount is in units of mg/m^2 and σ is in units of nm^{-2}. N_{Av} is Avogadro's number.

Parts A and B of Figure 1 are plots of the surface density and hydrodynamic layer thickness taken from Wu et al. for copolymers which fall in regime I. Parts A and B of Figure 2 are plots of the surface density and hydrodynamic layer thickness for copolymers falling in regime II. It can be seen that the surface density follows the MJ scaling predictions quite well, while some deviation is seen for the layer thickness, especially for the copolymer labeled a8b610. This material is the most asymmetric material reported in the study, having $\beta = 13.5$ (if a' is assumed to be 1). This places this polymer in the two-dimensional dilute regime discussed by Marques and Joanny.[1] In our studies of PS/PEO copolymers[3,4] we did not have such a highly asymmetric material available and thus were unable to verify the scaling predictions of MJ in that regime.

Parts A and B of Figure 3 compare the adsorbed amounts measured by Wu et al. with calculations using the MJ model for polymers with constant total degrees of polymerization of 700 and 200, respectively. In these model calculations the monomer sizes of both blocks have been assumed to be equal (i.e., $a' = 1$). The scaling model predicts the adsorbed amount to within a numerical prefactor of the order of unity, so there is one adjustable parameter in the fit. The same value of this parameter was used in both parts A and B of Figure 3. It is apparent that the model fits the measured values quite well. The model predicts that the adsorbed amount should pass through a maximum when $\beta = N_A^{1/2}$. The position of this maximum is close to that predicted by the model of Evers et al. It can be seen that the maxima in the experimental data lie slightly to the left of the maxima predicted by MJ in both parts A and B of Figure 3. Wu et al. also noted that the maxima in their data occurred to the left of the maxima predicted by Evers et al. and attributed this to

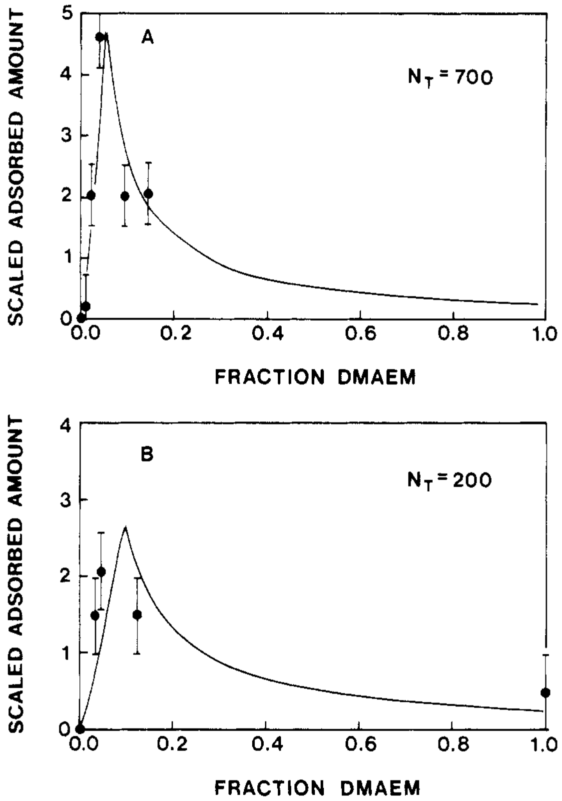

Figure 3. Comparison of experimental data of Wu et al.[6] with values of the adsorbed amount calculated from equations 1, 2, and 6 for total degrees of polymerization of (A) 700 and (B) 200.

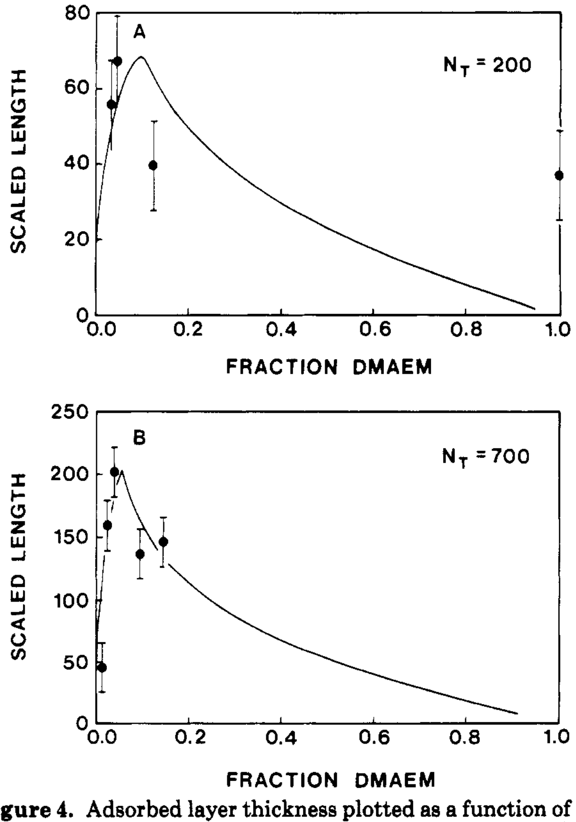

Figure 4. Adsorbed layer thickness plotted as a function of the mole fraction of the anchor polymer for (A) $N_T = 200$ and (B) $N_T = 700$. The solid line is the theoretical value determined from MJ. The closed circles are the experimental results of Wu et al.[6]

the polydispersity of the polymers. Both MJ and Evers et al. predict that the maxima will shift to the left if the molecular weights of the polymers are increased.

Parts A and B of Figure 4 compare the adsorbed layer thickness for $N_T = 200$ and $N_T = 700$, respectively, with the layer thicknesses predicted by MJ. Again there is only one adjustable parameter, and the model fit to the data is quite good. One deficiency of the model becomes apparent here, however, and that is that the scaling model cannot properly account for the thickness of the anchor layer without knowledge of the prefactors of the scaling laws. Thus at higher anchor block fractions, to the right in Figure 4, the fit to the model becomes poor because the anchor block thickness is ignored, while in a nonselective solvent the anchor block layer is negligible only for polymers with high β, i.e., low fractions of the anchor block.

It is apparent from the results of Wu et al. discussed above and our own work with PEO/PS copolymers that the scaling model of Marques and Joanny is a powerful tool for understanding block copolymer adsorption from a nonselective solvent. Thus, if a copolymer can be made which has one strongly interacting block and one nonadsorbing block in a nonselective solvent, the optimum polymer composition for maximum adsorbed amount and adsorbed layer thickness at a given total degree of polymerization can readily be calculated from $\beta = N_A^{1/2}$. This simple prediction of the model of Marques and Joanny may simplify the design of copolymers for stabilization.

References and Notes

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